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# **CLAIM + DETAILED DESCRIPTION**

[Claim(s)]

[Claim 1]

Dispersoid which has the metal-oxygen bond currently distributing stably under an acid, a base, and/or nonexistence of a dispersion stabilizing agent among an organic solvent without condensing.

[Claim 2]

Dispersoid which has a metal-oxygen bond of a description in the 1st paragraph of Claim to which dispersoid which has a metal-oxygen bond is characterized by being a hydrolysis product of metal alkoxide.

[Claim 3]

Dispersoid which has the metal-oxygen bond which is characterized by being obtained by hydrolyzing using water of less than a 0.5 to 1 time mole to metal alkoxide under an acid, a base, and/or nonexistence of a dispersion stabilizing agent among an organic solvent, and which is distributed stably without condensing among an organic solvent. [Claim 4]

Dispersoid which has the metal-oxygen bond currently distributed stably without condensing among an organic solvent obtaining at less than -20 \*\* under an acid, a base, and/or nonexistence of a dispersion stabilizing agent among an organic solvent by hydrolyzing using water of less than a 1.0 to 2.0 time mole to metal alkoxide. [Claim 5]

Dispersoid which has the metal-oxygen bond currently distributed stably without condensing among an organic solvent obtaining at -50--100 \*\* under an acid, a base, and/or nonexistence of a dispersion stabilizing agent among an organic solvent by hydrolyzing using water of less than a 1.0 to 2.0 time mole to metal alkoxide. [Claim 6]

[ metal oxide equivalent weight concentration of this dispersoid in a solution containing dispersoid which is produced by hydrolyzing metal alkoxide in a solvent, and which carries out a metal-oxygen bond owner ] Dispersoid which is 1.2 or more times and has the metal-oxygen bond currently distributing stably in a solvent to metal oxide equivalent weight concentration of metal alkoxide before a hydrolysis.

[Claim 7]

[ metal oxide equivalent weight concentration of this hydrolysis product in a solution containing dispersoid which has a metal-oxygen bond produced by hydrolyzing metal alkoxide in a solvent ] Dispersoid which is 1.4 or more times and has the metal-oxygen bond currently distributing stably in a solvent to metal oxide equivalent weight concentration of metal alkoxide before a hydrolysis.

[Claim 8]

Dispersoid which has a metal-oxygen bond of a description in Claim 6th or the 7th

paragraph, wherein a solvent is an organic solvent.

[Claim 9]

Dispersoid which has a metal-oxygen bond of a description in either of the 6-8th paragraphs of Claim to which dispersoid which has a metal-oxygen bond produced by hydrolyzing metal alkoxide in a solvent is characterized by being dispersoid which has a metal-oxygen bond of a description in either of the 2-5th paragraphs of Claim. [Claim 10]

Dispersoid which has a metal-oxygen bond of a description in either of the 6-8th paragraphs of Claim being obtained by condensing a solution of dispersoid which has a metal-oxygen bond of a description by either of the 2-5th paragraphs of Claim. [Claim 11]

Dispersoid which has a metal-oxygen bond of a description in either of the 1-10th paragraphs of Claim to which a solution containing dispersoid which has a metal-oxygen bond is characterized by an optically transparent thing.

[Claim 12]

Dispersoid which has a metal-oxygen bond of a description in the 2-11th paragraphs of Claim, wherein metal is one or more sorts chosen from a group which consists of titanium, zirconium, an aluminium, silicon, germanium, indium, tin, a tantalum, zirc, tungsten, and lead.

[Claim 13]

A metal oxide thin film being manufactured from dispersoid of a description by either of the 1-12th paragraphs of Claim.

[Claim 14]

A manufacturing method of a metal oxide thin film drying at temperature of 200 \*\* or less after applying a solution which contains dispersoid of a description in either of the 1-12th paragraphs of Claim.

[Claim 15]

A manufacturing method of a metal oxide thin film drying at temperature of 200 \*\* or less after applying a solution containing a metal oxide particle seed crystal derived to either of the 1-12th paragraphs of Claim from dispersoid and this dispersoid of a description.

[Claim 16]

A manufacturing method of a metal oxide thin film given in Claim 14th or the 15th paragraph irradiating with ultraviolet radiation with a wavelength of 360 more nm or less. [Claim 17]

Organic inorganic composite using as a mineral constituent inorganic polymer which uses as a starting material dispersoid which has a metal-oxygen bond of a description in either of the 1-12th paragraphs of Claim, or said dispersoid.

[Claim 18]

Organic inorganic composite given in the 17th paragraph of Claim, wherein an organic ingredient is at least one or more sorts chosen from a group which consists of acrylic resin, polythio urethane system resin, and resin obtained from an epithio group content compound.

[Claim 19]

An optical material by which organic inorganic composite of a description being included in Claim 17th or the 18th paragraph.

### [Claim 20]

Optical goods which become the 19th paragraph of Claim from an optical material of a description.

[Claim 21]

Optical goods given in the 20th paragraph of Claim, wherein optical goods are plastic lenses.

[Claim 22]

A manufacturing method of organic inorganic composite given in Claim 17th or the 18th paragraph polymerizing an organic monomer under existence of dispersoid which has a metal-oxygen bond of the 1-12th paragraphs of Claim.

## [Detailed Description of the Invention]

Technical field

This invention relates to the organic inorganic composite which uses as a component the inorganic polymer manufactured from the metal oxide thin film manufactured from the dispersoid which has a metal-oxygen bond, and this dispersoid and this dispersoid, or this dispersoid.

# Background art

The organic inorganic composite (called organic-inorganic matter hybrid and organic-inorganic matter compound polymer.) which made the mineral constituent decode in organic polymer attracts attention with the industrial material which has the new character to have organic polymer and the character of a mineral constituent. It is thought preferred to manufacture the organic inorganic composite for plastic lenses which has a high refractive index especially, and to use titanium oxide as a mineral constituent.

[ as an example of the organic inorganic composite using titanium oxide sol ] For example, in JP,H8-157735,A, [ under organic monomer existence ] An acid or a base is made into a catalyst for metal alkoxide, and the manufacturing method of organic-inorganic matter compound polymer carrying out [ a hydrolysis and ] polymerization of the organic inorganic composite which contains the metal oxide which made carry out dehydration condensation and was obtained with an organic monomer is indicated. To JP,H11-14949,A, at least Under a monomer and existence of this monomer, . Obtain metal alkoxide a hydrolysis and by carrying out dehydration condensation. The manufacturing method of the contact lens which polymerizes the monomer mixture containing the component B which is a monomer in which the monomer constituent of the component A and the component A which is a monomer constituent containing the metal oxide which may have an organic group, polyaddition, or polycondensation is possible is indicated.

As a manufacturing method of transparent and homogeneous metal oxide sol, for example, [JP,H10-298769,A] method \*\*\*\* which hydrolyzes and polymerizes one sort or two sorts or more of metal alkoxide, and manufactures metallic oxide precursor sol -- the manufacturing method of the metallic oxide precursor sol adding the water to said metal alkoxide at the temperature not more than -20 \*\* is indicated.

[ as a method of forming the thin film of a metal oxide on the surface of a substrate using

a sol-gel method ] After using metal alkoxide as a raw material, applying the sol obtained by hydrolyzing and polymerizing it and preparing substrate oxide precursor sol on the surface of a substrate and forming the thin film of a metal oxide gel in a substrate face, the method of heat-treating the gel membrane at a suitable temperature is known. By adding the organic compound in which polydent is possible among these methods, and stabilizing metal alkoxide, a hydrolysis rate can be controlled, the sol which can form membranes can be obtained, and the method of forming membranes in accordance with a described method using this sol can be illustrated preferably. Specifically, [ aluminium sbutoxide ] [ the formation of alumina membrane used as the starting material ] [ the formation of a titania thin film in which beta-diketone is effective (the Ceramic Society of Japan treatise magazine, 97, 396 (1989)), and used titanium isopropoxide as the starting material ] The thing (the Ceramic Society of Japan treatise magazine, 97, 213 (1989)) with effective beta-diketone is reported, respectively effectively [1,3-butanediol 1 (Hisao Koshiba, the Toyohashi University of Technology doctoral dissertation, Heisei 5(1993) March). It is reported by formation of the zirconia thin film which used zirconium n-butoxide as the starting material that use of diethylene glycol is effective (a ceramic industry association magazine, 95, 942 (1987)). Use of beta-diketone or alkanolamine is PbTiO<sub>3</sub> and Pb (). [ Zr and ] Ti), [ the report of being effective also in synthesis of multiple oxides, such as O<sub>3</sub>, ] It is indicated by journal OBU American ceramic SOSAIATI (Journal of American Ceramics Society), 74, 1407 (1991) and the Ceramic Society of Japan treatise magazine, and 98 and 745 (1990). A physics OBU Ching film (Physics of TinFilm), The report using the hydrolysis and aqua-complex of various mineral salt of a chloride, sulfate, nitrate, ammonium salt, etc. about the manufacturing method of an oxide film is made by 5, p87 (1969), and Academic Press (Academic Press). Using indium nitrate and chloridation tin instead of metal alkoxide for preparation of sol of In<sub>2</sub>O<sub>3</sub>-SnO<sub>2</sub> as a multiple oxide is shown in the Ceramic Society of Japan treatise magazine, and 102 and 200 (1994). However, also in which [ of JP,H8-157735,A and JP,H11-14949,A ] case, There was a problem that these which remain influenced a polymerization reaction from it being difficult to remove completely a hydrolysis, the water which carry out dehydration condensation, distills off a solvent, water, an acid, or a base, is carrying out bulk polymerization treatment, and was used, an acid, or a base for metal alkoxide using an acid or a base. Especially, in order to make the hydrolysis product of metal alkoxide exist stably in a solution, the acid, the base, or the dispersion stabilizing agent needed to be used for solution-polymerization \*\*\*\* in the inside of an organic solvent, and they also had the problem of having checked a polymerization or having a bad influence on the physical properties of a product in it. The above-mentioned inorganic - organic complex using a titanium oxide gel is in the tendency for permeability to be low, as compared with inorganic-organic complex using other metal oxide gels generally, and it can be referred to as having suggested that titanium oxide is condensing in the concentration stage after a hydrolysis and dehydration condensation.

Also in the transparent and homogeneous metal oxide sol in JP,H10-298697,A, pHs are acidic regions and there was the same problem as the point.

According to the method of stabilizing metal alkoxide by addition of the abovementioned polydent compound, and controlling the hydrolysis rate of metal alkoxide, although homogeneous sol for membrane formation can be prepared easily, many organic substances which are hard to disassemble in a high boiling point into sol or gel membrane will live together. As a result, it is necessary to heat-treat gel membrane at about 500 \*\* high temperature for removal of that organic substance. Since many organic substances remain in gel membrane, if gel membrane is heat-treated, membranous weight loss will become large. In other words, many pores are generated by removal of the organic substance from gel membrane in a film, and it becomes a cause of the defect of the obtained metal oxide thin film. That is, there were mechanical and a problem of a metal oxide that the various characteristics of optical and electric \*\* could not fully be demonstrated. On the other hand, in order to remove the pore in a film, energy excessive for elaboration of the thin film is needed. The method of using metal salt, as described above is a pyrolysis method fundamentally.

Many problems will be produced in the membraneous quality after heat-treatment.

While this invention provides metal oxide sol suitable for manufacture of the metal oxide thin film in the degree of low temperature of 200 \*\* or less, and manufacture of homogeneous organic inorganic composite, [ this invention ] It aims at providing the metal oxide thin film and organic inorganic composite which have various functions especially a high refractive index, and the organic inorganic composite which has high transparency.

The indication of an invention

[ by controlling the quantity of the water to be used, and reaction temperature, even if it does not use an acid, a base, or a dispersion stabilizing agent to metal alkoxide, as a result of this invention persons' inquiring wholeheartedly that the above-mentioned technical problem should be solved ] It finds out manufacturing the metal oxide sol which can be stably distributed in an organic solvent, forming a metal thin film further using this sol, and that a polymerization reaction can be carried out under sol existence, and homogeneous organic inorganic composite can be manufactured, and came to complete this invention.

Namely, this invention,

- (1) Dispersoid which has the metal-oxygen bond currently distributing stably under an acid, a base, and/or the nonexistence of a dispersion stabilizing agent among an organic solvent without condensing,
- (2) The dispersoid which has a metal-oxygen bond is related with the dispersoid which has a metal-oxygen bond of a description in (1) being a hydrolysis product of metal alkoxide.
- (3) Dispersoid which has the metal-oxygen bond which is characterized by being obtained by hydrolyzing using water of less than a 0.5 to 1 time mole to metal alkoxide under an acid, a base, and/or the nonexistence of a dispersion stabilizing agent among an organic solvent, and which is distributed stably without condensing among an organic solvent,
- (4) Dispersoid which has the metal-oxygen bond which is characterized by being obtained at less than -20 \*\* by hydrolyzing using water of less than a 1.0 to 2.0 time mole to metal alkoxide under an acid, a base, and/or the nonexistence of a dispersion stabilizing agent among an organic solvent, and which is distributed stably without condensing among an organic solvent,
- (5) Under the inside of an organic solvent, an acid, a base, and/or the nonexistence of a

dispersion stabilizing agent, -It is related with the dispersoid which has the metal-oxygen bond currently distributed stably without condensing among the organic solvent obtaining at 50--100 \*\* by hydrolyzing using water of less than a 1.0 to 2.0 time mole to metal alkoxide.

- (6), [ the metal oxide equivalent weight concentration of this dispersoid in the solution containing the dispersoid which is produced by hydrolyzing metal alkoxide in a solvent, and which carries out a metal-oxygen bond owner ] Dispersoid which is 1.2 or more times and has the metal-oxygen bond currently distributing stably in a solvent to the metal oxide equivalent weight concentration of metal alkoxide before a hydrolysis,
- (7), [ the metal oxide equivalent weight concentration of this hydrolysis product in the solution containing the dispersoid which has a metal-oxygen bond produced by hydrolyzing metal alkoxide in a solvent ] Dispersoid which is 1.4 or more times and has the metal-oxygen bond currently distributing stably in a solvent to the metal oxide equivalent weight concentration of metal alkoxide before a hydrolysis,
- (8) Dispersoid which has a metal-oxygen bond of a description in (6) to which a solvent is characterized by being an organic solvent, or (7),
- (9) Dispersoid to which the dispersoid which has a metal-oxygen bond produced by hydrolyzing metal alkoxide in a solvent has a metal-oxygen bond of a description in either of (2)(6) being dispersoid which has metal-oxygen bond of description in either of -(5) (8),
- (10) Dispersoid which has a metal-oxygen bond of a description in either of (2)(6) being obtained by either of (5) by condensing solution of dispersoid which has metal-oxygen bond of description (8),
- (11) Dispersoid which has a metal-oxygen bond of a description in either of (1) (10) to which the solution containing the dispersoid which has a metal-oxygen bond is characterized by an optically transparent thing,
- (12) Metal is related with the dispersoid which has a metal-oxygen bond of a description in (2) (11) being one or more sorts chosen from the group which consists of titanium, zirconium, an aluminium, silicon, germanium, indium, tin, a tantalum, zinc, tungsten, and lead.
- (13) It is related with the metal oxide thin film being manufactured from dispersoid of a description by either of (1) (12).
- (14) Manufacturing method of the metal oxide thin film drying at the temperature of 200 \*\* or less after applying the solution which contains dispersoid of a description in either of (1) (12),
- (15) A manufacturing method of a metal oxide thin film given in (14) drying at the temperature of 200 \*\* or less after applying the solution containing a metal oxide particle seed crystal,
- (16) It is related with the manufacturing method of a metal oxide thin film given in (14) irradiating with ultraviolet radiation with a wavelength of 360 more nm or less, or (15).
- (17) Organic inorganic composite using as a mineral constituent the inorganic polymer which uses as a starting material the dispersoid which has a metal-oxygen bond of a description in either of (1) (12), or said dispersoid,
- (18) An organic ingredient is related with organic inorganic composite given in (17) being at least one or more sorts chosen from the group which consists of acrylic resin, polythio urethane system resin, and resin obtained from an epithio group content

compound.

An optical material by which the organic inorganic composite of a description being included in (19), (17), or (18),

Optical goods set to (20) and (19) from the optical material of a description, (21) optical goods are related with optical goods given in (20) being a plastic lens -- further

(22) It is related with the manufacturing method of organic inorganic composite given in (17) polymerizing an organic monomer or (18) under existence of the dispersoid which has a metal-oxygen bond of (1) - (12).

Dispersoid in this invention is stably distributed under an acid, a base, and/or the nonexistence of a dispersion stabilizing agent among an organic solvent, without condensing.

In this case, dispersoid can mean the microscopic particles currently distributed in a dispersed system, and, specifically, a colloidal particle etc. can be illustrated. An organic solvent will not be limited especially if an organic substance can distribute dispersoid, but specifically, Alcoholic solvent, such as methanol, ethanol, and isopropyl alcohol, Chlorine-based solvents, such as a methylene chloride and chloroform, hexane, cyclohexane, Hydrocarbon system solvents, such as benzene, toluene, xylene, and chlorobenzene, Ether system solvents, such as tetrahydrofuran, diethylether, and dioxane, Ketone solvent, such as acetone, methyl ethyl ketone, and methyl isobutyl ketone, Aprotic polar solvents, such as dimethylformamide, dimethyl sulfoxide, and Nmethylpyrrolidone, The methylpolisiloxane used for the dispersion medium of the titanium dioxide dispersing element indicated to JP,H9-208438,A, So that silicone, such as octamethylcyclotetrasiloxane, decamethyl cyclopentane siloxane, and methylphenyl polysiloxane, etc. can be illustrated and it may mention later, In order to perform the hydrolysis reaction using water at low temperature, the solubility of water is large, the solvent which is not solidified at low temperature is preferred, and a lower alcohol system solvent, an ether system solvent, etc. can specifically be illustrated preferably. These solvents are one-sort independent, or can mix two or more sorts and can be used. [ the acid or base used in this Description ] So that it may solidify and may mention later by making completed precipitate into the deflocculatant distributed again, Metal alkoxide etc., [ as a hydrolysis and a catalyst for carrying out dehydration condensation and manufacturing dispersoid, such as a colloidal particle, And especially if it functions as a dispersant of the generated dispersoid, will not be restricted, but as an acid specifically, Mineral acids, such as hydrochloric acid, nitric acid, boric acid, and fluoroboric acid, acetic acid, formic acid, oxalic acid, Can illustrate organic acids, such as carbonic acid, trifluoroacetic acid, p-toluenesulfonic acid, and methanesulfonic acid, etc., and further, The photo-oxide generating agent and concrete target which generate an acid by light irradiation can illustrate diphenyliodonium hexafluorophosphate, triphenyl phosphonium hexafluorophosphate, etc. Triethanolamine, triethylamine, 1,8-diazabicyclo [5, 4, 0]-7undecene, ammonia, phosphine, etc. can be illustrated as a base.

The dispersion stabilizing agent used into this Description refers to the component made to add in order to distribute dispersoid in a dispersion medium as stably as possible, and shows coagulation inhibitors, such as a defloculatant, protective colloid, and a surface active agent, etc. As a compound which it has, such an operation specifically, What a chelated compound can be illustrated, and at least one carboxyl group is contained in the

molecular skeleton, and has a strong chelate effect to metal is preferred, and, [ as such a compound ] Polyvalent carboxylic acid, such as glycolic acid, gluconic acid, lactic acid, tartaric acid, citric acid, malic acid, and succinic acid, or hydroxycarboxylic acid can be illustrated, and pyrophosphoric acid, Tripoli phosphoric acid, etc. can be illustrated further. [ as a multidentate ligand compound which similarly has strong chelating ability power to a metal atom ] Acetylacetone, methyl acetoacetate, ethyl acetoacetate, acetoacetic acid-n-propyl, Acetoacetic acid-i-propyl, acetoacetic acid-n-butyl, acetoacetic acid-sec-butyl, Acetoacetic acid-t-butyl, 2,4-hexane-dione, 2,4-heptane-dione, 3,5heptane-dione, 2,4-octane-dione, 2,4-nonane-dione, 5-methyl-hexane-dione, etc. can be illustrated, in addition, [ as a fatty amine system, a hydro-stearic acid system, and polyesteramine | Sour Perth 3000, 9000, 17000, 20000, and 24000 (above) The Zeneka Co. make, Disperbyk-161, -162, -163, -164 (above) Can illustrate the product made by big KEMI, etc. and JP,H9-208438,A, The dimethylpolysiloxane methyl (polysiloxy alkylene) siloxane copolymer indicated to JP,H2000-53421,A etc., Silicone compounds, such as trimethylsiloxy silicic acid, carboxy denaturation silicone oil, and amine denaturation silicone, etc. can be illustrated.

Among an organic solvent, the state in this invention where it is distributing stably without condensing expresses the state where the dispersoid which has a metal-oxygen bond solidifies and has not dissociated heterogeneously, and expresses a state it is desirable and transparent and homogeneous. In this case, the permeability in visible light says transparence and a high state specifically, Concentration of dispersoid shall be made into 0.5 weight % by oxide conversion, the optical path length of a quartz cell shall be 1 cm, an object sample is used as an organic solvent, and the state of expressing with the spectral transmittance measured on the conditions which set wavelength of light to 550 nm, and expressing the permeability of 80 to 100% preferably is said. Although the particle diameter in particular of dispersoid of this invention is not limited, in order to obtain the high permeability in visible light, it is preferred to make the particle diameter into the range of 1-100 nm, and it is preferred to consider it as the range of 1-50 nm and further 1-10 nm.

the manufacturing method of the dispersoid which has a metal-oxygen bond in this invention ] If it will not be limited especially if the dispersoid which has the above character is obtained, for example, titanium is mentioned as an example as a metal atom, The method of hydrolyzing with water organic titanium compounds which neutralize inorganic titanium compounds, such as a titanium chloride, oxy-salt-ized titanium, titanium sulfate, and titanyl sulfate, by a suitable base after a hydrolysis if needed with water, such as a method and titanium alkoxide, etc. can be illustrated. The method of hydrolyzing metal alkoxide can be preferably illustrated as a manufacturing method of the dispersoid which has a metal-oxygen bond which can be distributed especially stably. As a metal atom used for this invention, specifically, the [ the alkali metal from the 2nd period of the periodic table to the 6th period, an alkali earth metal element, and ] -- 3B group element. the [from the 3rd period of the periodic table to the 6th period] -- the [ 4B group element and ] -- the combination of one sort or two sorts or more of metal of the element chosen from the group which consists of 5B group element, a transition metal element, and lanthanoids can be illustrated. In particular, the case of titanium, zirconium, an aluminium, silicon, germanium, indium, tin, a tantalum, zinc, tungsten, and lead is preferred.

As a raw material for manufacturing the dispersoid which has a metal-oxygen bond in this invention, specifically, Si(OCH<sub>3</sub>) 4, Si(OC<sub>2</sub>H<sub>5</sub>) 4, Silicon alkoxide, such as Si(i-OC<sub>3</sub>H<sub>7</sub>) 4 and Si(t-OC<sub>4</sub>H<sub>9</sub>) 4, Ti(OCH<sub>3</sub>) 4, Ti(OC<sub>2</sub>H<sub>5</sub>) 4, Titanium alkoxide, such as Ti(i-OC<sub>3</sub>H<sub>7</sub>) 4 and Ti(OC<sub>4</sub>H<sub>9</sub>) 4, Zr(OCH<sub>3</sub>) 4, Zr(OC<sub>2</sub>H<sub>5</sub>) 4, Zirconium alkoxide, such as Zr(OC<sub>3</sub>H<sub>7</sub>) <sub>4</sub> and Zr(OC<sub>4</sub>H<sub>9</sub>) <sub>4</sub>, aluminum(OCH<sub>3</sub>) <sub>3</sub>, aluminum(OC<sub>2</sub>H<sub>5</sub>) <sub>3</sub>, Germanium alkoxide, such as aluminium alkoxide, such as aluminum(i-OC<sub>3</sub>H<sub>7</sub>)<sub>3</sub> and aluminum( $OC_4H_9$ ) 3, and germanium( $OC_2H_5$ ) 4, In( $OCH_3$ ) 3, In( $OC_2H_5$ ) 3, In( $I-OC_3H_7$ ) 3, Indium alkoxide, such as In(OC<sub>4</sub>H<sub>9</sub>) <sub>3</sub>, Sn(OCH<sub>3</sub>) <sub>4</sub>, Sn(OC<sub>2</sub>H<sub>5</sub>) <sub>4</sub>, Tin alkoxide, such as Sn(i-OC<sub>3</sub>H<sub>7</sub>) 4 and Sn(OC<sub>4</sub>H<sub>9</sub>) 4, Ta(OCH<sub>3</sub>) 5, Ta(OC<sub>2</sub>H<sub>5</sub>) 5, Tantalum alkoxide, such as Ta(i-OC<sub>3</sub>H<sub>7</sub>) <sub>5</sub> and Ta(OC<sub>4</sub>H<sub>9</sub>) <sub>5</sub>, W(OCH<sub>3</sub>) <sub>6</sub>, W(OC<sub>2</sub>H<sub>5</sub>) <sub>6</sub>, Tungsten alkoxide, such as  $W(i-OC_3H_7)$  6 and  $W(OC_4H_9)$  6, Lead alkoxide, such as zinc alkoxide, such as  $Zn(OC_2H_5)$ 2, and Pb(OC<sub>4</sub>H<sub>9</sub>) 4, is mentioned. It is contained in the metal alkoxide which also uses the partial hydrolysate of metal alkoxide of the above-mentioned illustration by this invention. It may be the complex alkoxide obtained by a reaction with the complex alkoxide obtained by the reaction between metal alkoxide of two or more sorts of said elements, one sort, or two sorts or more of metal alkoxide, one sort, or two sorts or more of metal salt. It is also possible to use it combining these.

As complex alkoxide obtained by the reaction between two or more sorts of metal alkoxide, specifically, The complex alkoxide obtained by the reaction of alkoxide of an alkali metal or an alkaline earth metal, and alkoxide of a transition metal, the -- the complex alkoxide as a complex salt obtained with the combination of 3B group element being illustrated, and more specifically, BaTi(OR) 6, SrTi(OR) 6, BaZr(OR) 6, SrZr(OR) 6, LiNb(OR) 6, LiTa(OR) 6 and these combination, LiVO(OR) 4, and MgAl2(OR) 8 etc. can be illustrated. (RO) 3SiOAl(OR') 2, (RO) 3SiOTi(OR') 3, (RO) 3SiOZr(OR') 3, (RO) 3SiOB(OR') 2, (RO) A reactant and its condensation polymer with silicon alkoxide, such as 3SiONb(OR') 4 and (RO) 3SiOTa(OR') 4, can be illustrated further. Here, R and R' shows an alkyl group. The compound obtained by the reaction of metal salt, such as a chloride, nitrate, sulfate, acetate, formate, and oxalate, and alkoxide can be illustrated as complex alkoxide obtained by a reaction with one sort or two sorts or more of metal alkoxide, one sort, or two sorts or more of metal salt.

Although the carbon number in particular of the alkoxy group of metal alkoxide is not limited, content oxide concentration, the ease of desorption of an organic substance, the ease of acquisition, etc. to the carbon numbers 1-4 are more preferred. Instead of an alkoxy group, it is necessary to neutralize more the carboxylic acid which generates a hydrolysis after a hydrolysis although acyloxy groups, such as an easy acetoxy group, can also be used.

Metal alkoxide illustrated as mentioned above,

- (1) Use water of less than a 0.5 to 1.0 time mole to metal alkoxide under an acid, a base, and/or the nonexistence of a dispersion stabilizing agent among an organic solvent, (2) the bottom of the inside of an organic solvent, an acid, a base, and/or the nonexistence
- (2) the bottom of the inside of an organic solvent, an acid, a base, and/or the nonexistence of a dispersion stabilizing agent, and-it is the range of -50--100 \*\* preferably, and use 20 \*\* or less of water of less than a 1.0 to 2.0 time mole to metal alkoxide

The dispersoid which has a metal-oxygen bond which can be distributed stably by one which is said of methods without condensing in an organic solvent can be manufactured. After hydrolyzing at arbitrary temperature using the quantity of the water set up above (1), it can also react by adding the quantity of water further under the temperature

conditions set up by the above (2).

Especially if the water to be used is neutral, it will not be restricted, but it is preferred to use pure water or distilled water, and especially if the quantity is the range which specified [ above-mentioned ], it will not be restricted, but it can be arbitrarily chosen by the dispersoid which has the target character.

Although the reaction of metal alkoxide and water in the above (1) can also be performed in an organic solvent, it can also carry out by mixing water with direct metal alkoxide, without using an organic solvent.

[ the reaction of metal alkoxide and water in the above (2) ] In the method of adding the water diluted with the organic solvent to the organic solvent solution of metal alkoxide, and the organic solvent which water suspended for which or dissolved, although it can carry out by metal alkoxide or the method of adding the dilution solution of an organic solvent, and any method, the method of adding water later is preferred.

The concentration in metal alkoxide or the organic solvent of water controls rapid generation of heat, especially if it is a range which has the flowability which can be agitated, it will not be limited, but it is usually preferred to carry out in the density range of 5 to 30weight % of metal alkoxide.

In the reaction of metal alkoxide and water in the above (1), the reaction temperature in particular is not restricted, but can be performed in -100-100 \*\*, and is usually performed in the range of the boiling point of the alcohol from which it is desorbed according to a room temperature - a hydrolysis.

In the reaction of metal alkoxide and water in the above (2), the reaction temperature is dependent on the stability of metal alkoxide.

-Especially if it is 20 \*\* or less in temperature, it will not be limited, but it is more preferred to add the water to metal alkoxide in [ temperature ] -50 \*\*--100 \*\* depending on the kind of metal alkoxide.

After adding water and carrying out definite-period-of-time aging at low temperature, a hydrolysis and a dehydrating condensation reaction can also be further performed at the flowing-back temperature of the solvent used from the room temperature. -, without adding dispersion stabilizing agents, such as a polydent compound, and stabilizing metal alkoxide hydrolyzate by adding water at the low temperature of 20 \*\* or less, It becomes possible about metal alkoxide to perform a hydrolytic polymerization reaction at high concentration, and the high-concentration dispersion liquid which do not contain unnecessary organic substances, such as a polydent compound, can be obtained. As a result, when these dispersion liquid were used, gel membrane with few organic matter contents, a gel fiber, a bulk gel, etc. are obtained and an organic substance is desorbed from those gels by heat-treatment etc., the destruction and the remains pore amount of fine texture in the acquired Plastic solid can be reduced.

[ this invention ] [ the metal oxide equivalent weight concentration of this dispersoid in the solution containing the dispersoid which has the metal-oxygen bond which was prepared as mentioned above, and which is produced by hydrolyzing metal alkoxide in a solvent ] To the metal oxide equivalent weight concentration of metal alkoxide before a hydrolysis, 1.2 or more times, even if it is further 1.4 or more times, it is distributing stably in a solvent. Also in [ as for this, beyond a room temperature distills off an organic solvent for the solution which the dispersoid which has a metal-oxygen bond in an organic solvent distributed to high concentration below 80 \*\* preferably further, and ] a

further high-concentration state, Even if it means that dispersoid particles do not solidify and adds an organic solvent again, it becomes homogeneous and transparent dispersion liquid. With a high-concentration state, the state at that time can take one states of solid state voice, a liquid state, and a gelling state, or these mixed state with metal including the state where there is no solvent.

A metal oxide thin film and organic inorganic composite can be manufactured from the inorganic polymer which uses as a starting material the dispersoid which has the metal-oxygen bond prepared as stated above, and/or said dispersoid.

About the manufacturing method of a metal oxide thin film, the solution containing said dispersoid is dried at the temperature of 200 \*\* or less after spreading.

Although the concentration of dispersoid in the solution containing said dispersoid changes also with thickness made into a coating method and the purpose, especially if it is the concentration which can be applied on a substrate, it will not be restricted, but, specifically, 5 to 50weight % of its range is preferred by the weight converted into the oxide.

Although it is preferred to use the same solvent as the solvent used for being able to illustrate the solvent used for distributing said dispersoid and the same solvent, and distributing said especially dispersoid as a solvent used for a solution, different solvents can also be used if it is a solvent which does not affect the dispersibility of dispersoid. In the solution containing said dispersoid, other components can be added if needed. As other components, specifically Silicon compounds, such as water glass, colloidal silica, and polyorganosiloxane, Phosphate, such as zinc phosphate and aluminium phosphate, heavy phosphate, cement, Lime, gypsum, the frit for enamel, the glaze for glass linings, Inorganic system binders, such as plaster, fluorine system polymer, silicon system polymer, Organic system binders, such as an acrylate resin, an epoxy resin, polyester resin, a melamine resin, urethane resin, and an alkyd resin, etc. are mentioned, and these binders can be used combining single or two sorts or more. In particular, the inorganic system binder from a viewpoint of adhesive strength, fluorine system polymer, and silicon system polymer are preferred. As cement, for example High-early-strength cement, common cement, moderate-heat cement, Blended cement, such as Portland cement, such as sulfate resisting cement, white (white) cement, oil well cement, and geothermal cement, fly ash cement, high sulfate cement, pozzolanic cement, and Portland blast furnace cement, an alumina cement, etc. can be used. As plaster, a gypsum plaster, lime plaster, dolomite plaster, etc. can be used, for example. As fluorine system polymer, for example Polyvinyl fluoride, polyvinylidene fluoride, Poly ethylene trifluoride chloride, polytetrafluoroethylene, a polytetrafluoroethylene propylene hexafluoride copolymer, An ethylene-polytetrafluoroethylene copolymer, an ethylene-ethylene trifluoride chloride copolymer, Crystalline fluororesins, such as tetrafluoroethylene perfluoroalkyl vinyl ether copolymer, Amorphous fluorocarbon resin, such as perfluoro cyclo polymer, a vinyl ether fluoro olefin copolymer, and a vinyl ester fluoro olefin copolymer, various kinds of fluorine system rubber, etc. can be used. Since [ with little / and / fluorine system polymer to decomposition and deterioration which made the principal component especially the vinyl ether fluoro olefin copolymer and the vinyl ester fluoro olefin copolymer | handling is easy, it is desirable. As silicon system polymer, silicon modified resins, such as straight chain silicon resin, acrylic modification silicon resin, acrylic silicon resin, and epoxy-silicon resin, various kinds of silicon system

rubber, etc. can be used.

The ratio of other components which illustrated [above-mentioned] with said dispersoid is weight %, and is 70 to 98% 50 to 98% 20 to 98% preferably 5 to 98%. A thermostabilizer, an antioxidant, an ultraviolet ray absorbent, an antistatic agent, a colorant, a surface active agent, a cross linking agent, a dispersant, a bulking agent, etc. can be combined with the solution containing said dispersoid if needed. As a cross linking agent, the usual cross linking agents, such as an isocyanate system and a melamine system, can be used for a coupling agent etc. as a dispersant. Specifically, each publicly known method, such as a spin coat method, a dip coating method, a spray coating method, the roll coat method, and screen printing, can use it as a method of applying the solution which contains said dispersoid in a base. In order to mass-produce inexpensive, the roll coat method is preferred. Especially the method of using a bar and the method of using GISA are a desirable method. Screen printing and offset printing are also preferred at the point that patterning is possible at the time of spreading. Although coverage changes with uses of the thin film obtained, it is generally  $0.1 - 10 \text{ ml/m}^2$  as amounts of \*\*\*\*\*\*\*\* other than a solvent. More preferably, it is 0.2- 7 ml/m<sup>2</sup> and is 0.4 - 5 ml/m<sup>2</sup> still more preferably.

As a base, the article of quality of a metallic material, such as alloys, such as metal, such as an article of the organic quality of the materials, such as an article of quality of nonequipments, such as Ceramics Sub-Division and glass, plastics, rubber, a tree, and paper, and an aluminium, and steel, can be used. It is not restricted to in particular the size or form of a base, but a plate, a solid thing, a film, etc. can use all. The painted article can also be used. Especially, the film of plastics has it and, [preferred] [as an example] Cellulose triacetate, cellulose diacetate, cellulose nitrate, Polystyrene, polyethylene terephthalate, polyethylenenaphthalate, syndiotactic polystyrene, polyethylene covering paper, polyether sulphone, polyarylate, polyvinylidene fluoride, Teflon, etc. can be used. The water resistant layer containing polyvinylidene chloride system polymer may be provided in order to improve what is called dimension stability from which a size changes with change of temperature or humidity to these base materials. The thin film of organicity and/or an inorganic compound may be provided for the purpose of a gas barrier. Polyvinyl alcohol, poly (ethylene-co-vinyl alcohol), etc. are raised as an example of an organic thin film, and silica, alumina, a tale, a vermiculite, kaolinite, mica, synthetic mica, etc. are mentioned as an example of an inorganic compound. In addition, various organicity and/or an inorganic additive may be added into the substrate for many functions.

With desiccation of a solvent, heating of a spreading film is performed for a hydrolysis of said dispersoid, and dehydration condensation. As for the heating conditions after spreading, it is preferred to be carried out at low temperature 200 \*\* or less in order not to give a damage to a substrate. Preferably, it is carried out at 20 \*\* - 100 \*\*. It is carried out at 30 \*\* - 80 \*\* still more preferably. Although heat time in particular is not limited, 1 minute - 120 hours are usually performed suitably.

What is necessary is just to form an overcoat on this thin film in this invention, when the mechanical strength of the formed thin film is required. When forming this overcoat, the usual coating liquid for overcoat formation, for example, the coating liquid for silica based film formation containing alkoxysilane hydrolyzate, is used.

In the case of the metal oxide thin film which needs crystallization, in this invention, it is

preferred that the metal oxide particle seed crystal used as the coating liquid containing the dispersoid which has a metal-oxygen bond with the purpose is added. The addition percentage of a metal oxide particle seed crystal is 10wt% - of sol weight [ when sol generates from said dispersoid ], and 90wt% preferably.

It is 10wt% - 80wt% especially preferably.

In this invention, a metal oxide may crystallize by light irradiation so that it may state later, but the seed crystal is added in this case.

Therefore, crystallization of a metal oxide promotes further.

Although the size of a seed crystal is arbitrary, 0.1 micrometer or less is preferred at the viewpoint of permeability to ball conversion.

even if the seed crystal to add is not the metal oxide itself made into the purpose -- a crystal form -- the same -- and/or, hetero, such as what takes a value with a near grating constant, -- what has good convenience can also be used epitaxial. For example, when creating an ITO thin film, indium oxide can be used as a seed crystal.

The compound thing may be used for it even if a commercial item is used for an above-mentioned seed crystal. When a metal oxide thin film is ITO, in a commercial item, the MITSUBISHI MATERIALS make, the Sumitomo Metal Mining thing, etc. can be used. About a synthetic process, other usual sintering of a sol-gel method and hydrothermal synthesis, etc. are mentioned. "A sol-gel method The science of a sol-gel method, Sumio Sakuhana, the company of the AGUNE \*\* style, It is described in detail by 1988", "the thin-layer-coating art by a sol-gel method, edited by TECHNICAL INFORMATION INSTITUTE and 1994", "the present condition of a sol-gel method, a view, Masayuki Yamane editorial supervision, the technical information service round-table conference [ATIS] sol-gel method report publication meeting, 1992", etc.

In the method for forming thin film of this invention, it is preferred to carry out light irradiation after the time of heating of a coating film and/or heating. As long as light with a wavelength of 150 nm - 700 nm is generated, what kind of thing may be used for the light source which irradiates a spreading film with ultraviolet radiation or visible light. For example, an extra-high pressure mercury lamp, a high pressure mercury lamp, a low pressure mercury lamp, a xenon lamp, a halogen lamp, a sodium lamp, etc. are mentioned. Preferably, they are an extra-high pressure mercury lamp, a high pressure mercury lamp, a low pressure mercury lamp, and a xenon lamp. A transparent conductive pattern can be formed by using a photomask together. A laser oscillation device can also be used. As a laser oscillation device, an excimer laser, argon laser, a helium neon laser, a semiconductor laser, an YAG laser, carbon dioxide laser, dye laser, etc. are mentioned. Since it does not change with a metal oxide other than irradiation portions when a laser beam is used, pattern formation is possible, without using screen-stencil etc. at the time of spreading. Synchrotron radiation can also be used. These devices can be chosen in consideration of wavelength to irradiate with. When the coating liquid containing said dispersoid is reacted, it is good for generation of a metal oxide to use the device which generates ultraviolet radiation \*\*\*\*\* of 400 nm or less in consideration of absorption of this metal-OH binding, although metal hydroxide also remains. When dehydration advances and a metalaw KISAN network forms, although absorption of a metal-Ometallic bond is short wavelength, crystallization of a metal oxide promotes it from metal-OH binding by the light irradiation of the wavelength which can activate a metalO-metallic bond. Although irradiation time in particular is not limited, 1 minute - 120 hours are usually performed suitably.

In this invention, although the atmosphere in a light irradiation process is liberal, it is preferred to carry out by a certain amount of reducing atmosphere. Under a certain amount of reducing atmosphere, it is thought that increase of the carrier density by increase of an oxygen defect and/or adsorption of the oxygen molecule to a grain boundary were controlled.

On the other hand, the high boiling point low-molecular-weight solvent disassembled by light irradiation may be used. Isophorone and benzyl acetate are mentioned as such an example.

As what can be added, when performing light irradiation in the solution containing said dispersoid, resin made from photodisintegration, etc. can be used for it. For example, polymethyl vinyl ketone, polyvinyl phenyl ketone, polysulfone, Diazonium salts, such as p-diazodiphenylamine paraformaldehyde polycondensation thing, Quinone diazide, such as 1,2-naphthoquinone 2-diazido 5-sulfonic acid isobutyl ester, polymethylmethacrylate, polyphenyl methylsilane, poly methyliso propenyl ketone, etc. are mentioned. In the case of the above-mentioned resin, it is desirable to use it at a rate of zero to 1000 weight section per a total of 100 weight sections of metal alkoxide or metal salt.

When performing light irradiation and the absorption wavelengths of irradiation light wavelength, metal alkoxide, metal salt, and/or these chelate compound differ, it is good to add a photosensitizer to the liquid containing metal alkoxide and/or metal salt as other additives.

After applying on a base the solution containing said dispersoid, especially if it is 200 \*\* or less, it will not be restricted as a temperature to dry, but it is preferred to make it dry below 150 \*\* preferably.

Among organic inorganic composite, especially as an organic ingredient, it is not limited, and both an addition polymer a polyaddition object and a polycondensation body can use resin, and it can specifically illustrate it below.

The monomer described below is used as a raw material as acrylic resin, and what polymerized this is mentioned. As monofunctional methacrylic acid ester, methyl methacrylate, ethyl methacrylate, Methacrylic acid n-butyl, hexyl methacrylate, benzyl methacrylate, Phenyl methacrylate, cyclohexyl methacrylate, methacrylic acid isobornyl, methacrylic acid adamanthyl, etc. are mentioned, and, [ as polyfunctional methacrylic acid ester | Ethylene glycol dimethacrylate, diethylene glycol dimethacrylate, Triethylene glycol dimethacrylate, tripropylene dimethacrylate, 1,4-butanediol dimethacrylate, 1,6hexanedioldimethacrylate, Trimethylolpropanetrimethacrylate, pentaerythritol trimethacrylate, glycerol dimethacrylate, 2,2-bis[4-(meta-KURIROKISHI) phenyl] propane, 2,2-bis[4-(meta-KURIROKISHI ethoxy) phenyl] propane, etc. are mentioned. As monofunctional acrylic ester, methyl acrylate, ethyl acrylate, They are mentioned by acrylic acid n-butyl, hexyl acrylate, cyclohexyl acrylate, benzyl acrylate, phenyl acrylate, acrylic acid isobornyl, etc., and, [ as polyfunctional acrylic ester ] Ethylene glycol diacrylate, triethylene glycol diacrylate, 1, 6-hexanediol diacrylate, trimethylolpropane triacrylate, pentaerythritol bird acrylate, etc. are mentioned. [ as an above-mentioned acrylic or an methacrylic compound, and a copolymerizable monomer ] Styrene, methylstyrene, dimethylstyrene, KURORU styrene, dichloro styrene, Nuclear substitution styrene and alpha-methylstyrene, such as bromine styrene, p-KURORU

methylstyrene, and divinylbenzene, There are acrylonitrile, methacrylonitrile, maleic anhydride, N-substitution maleimide, etc., and these, an above-mentioned acrylic, or a copolymer with an methacrylic compound also corresponds to acrylic resin. The organic monomer in which a radical or cationic polymerization is possible is preferred, and especially the organic monomer containing at least one sort of bindings chosen from an amide bond, imide bonding, a urethane bond, and an urea bond is preferred. [ as an example of the organic monomer in which a radical polymerization is possible among such organic monomers ] (Meta) The adduct of acrylamide, acrylamide

possible among such organic monomers ] (Meta) The adduct of acrylamide, acrylamide derivatives (meta), acryloyl morpholine (meta), N-vinyl pyrrolidone, urethane acrylate (meta), amino alkyl (meta) acrylate, and an isocyanate, etc. are mentioned. As for acrylamide (meta), acrylate shows both methacrylate and acrylate for both methacrylamide and acrylamide here again (meta).

On the other hand, as a monomer in which cationic polymerization is possible among the above-mentioned organic monomers, the compound which has an epoxy ring, vinyl ether binding, and an alt.spiro loop as a polymerization functional group is mentioned. With the above-mentioned indispensable organic monomer, an arbitrary organic monomer may be used for reforming of the polymer which can be obtained, and even if this kind of arbitrary organic monomer has an amide bond, a urethane bond, and an urea bond, it does not need to be. However, that polymerization form (a radical polymerization, cationic polymerization) of this arbitrary organic monomer must be the same as that of the above-mentioned indispensable monomer.

[ as an example of such an arbitrary organic monomer ] When an indispensable monomer is a radical polymerization nature monomer, methyl (meta) acrylate, Tricyclo [5, 2, 1, 0] deca nil (meta) acrylate, neopentyl glycol di(metha)acrylate, 3,3,3-trifluoroethyl (meta) acrylate etc. are mentioned, and when an indispensable monomer is a cation pile affinity monomer, ethylene glycol diglycidyl ether, propylene glycol diglycidyl ether, \*\*\*\* bisphenol A diglycidyl ether, etc. are mentioned.

Poly (thio) urethane system resin means polythio urethane or polyurethane system resin obtained by a reaction with a polyisocyanate compound, a polythiol compound, or a polyhydroxy compound.

Especially as a polyisocyanate compound, it is not limited but the following can be mentioned as the example.

- (i) \*\*\*\* 2,6-tolylene diisocyanate, \*\*\*\* meta, and the Para Feni range isocyanate, Alicycle group isocyanate compounds, such as \*\*\*\* 2,4-tolylene diisocyanate, hydro-diphenylmethane diisocyanate, \*\*\*\* meta-xylylene diisocyanate, \*\*\*\* PARAKI silylene diisocyanate, and isophorone diisocyanate,
- (ii) Meta and the Para Feni range isocyanate, 2, 4-tolylene diisocyanate, 2, 6-tolylene diisocyanate, 4, and 4'-diphenylmethane diisocyanate, Meta and PARAKI silylene diisocyanate, meta, and PARATE truck methylxylylene diisocyanate, the isocyanate compound (a desirable thing -- 2 and 4- and 2, and 6-tolylene diisocyanate.) which has aromatic rings, such as 2,6-naphthalene diisocyanate and 1,5-naphthalene diisocyanate 4,4'-diphenylmethane diisocyanate, meta-xylylene diisocyanate, meta-tetramethyl xylylene diisocyanate, 2,6-naphthalene diisocyanate, etc.,
- (iii) Hexamethylene di-isocyanate, octamethylene diisocyanate, 2, 2, 4-trimethyl hexamethylene di-isocyanate, tetramethylene di-isocyanate, The BYUU let resultant of hexamethylene di-isocyanate, the trimer of hexamethylene di-isocyanate, The isocyanate

compound which does not have alicycle, such as lysine diisocyanate, lysine triisocyanate, and 1,6,11-undecane TORIISOSHIANETOTORI phenylmethane tri-isocyanate, and an aromatic ring,

(iv) Diphenyldisulfide 4,4'-diisocyanate, 2,2'-dimethyldi phenyldisulfide 5,5'diisocyanate, 3,3'-dimethyldi phenyldisulfide 5,5'-diisocyanate, 3,3'-dimethyldi phenyldisulfide 6,6'-diisocyanate, 4,4'-dimethyldi phenyldisulfide 5,5'-diisocyanate, 3,3'dimethoxy diphenyldisulfide 4,4'-diisocyanate, 4,4'-dimethoxy diphenyldisulfide 3,3'diisocyanate, Diphenylsulfone 4,4'-diisocyanate, diphenylsulfone 3,3'-diisocyanate, Benzyliene sulfone 4,4'-diisocyanate, diphenylmethane sulfone 4,4'-diisocyanate, 4methyldi phenyl methanesulfon 2,4'-diisocyanate, 4,4'-dimethoxy diphenylsulfone 3,3'diisocyanate, 3,3'-dimethoxy-4,4'-diisocyanatodibenzylsulfone, 4,4'-dimethyl diphenylsulfone 3,3'-diisocyanate, 4,4'-di-tert-butyl diphenylsulfone 3,3'-diisocyanate, 4,4'-dimethoxybenzene ethylenedisulfon 3,3'-diisocyanate, 4,4'-dichloro diphenylsulfone 3,3'-diisocyanate, 4-methyl-3-isocyanato benzenesulfonil 4'-isocyanatophenol ester, 4methoxy-3-isocyanato benzenesulfonil 4'-isocyanatophenol ester, 4-methyl-3-isocyanato benzenesulfonil anilide 3'-methyl-4'-isocyanate, Dibenzene sulfonyl ethylene diamine 4,4'-diisocyanate, 4,4'-dimethoxybenzene sulfonyl ethylene diamine 3,3'-diisocyanate, 4methyl-3-isocyanato benzenesulfonil anilide 4-methyl-3'-isocyanate, Thiophene 2,5diisocyanate, thiophene 2,5-diisocyanatomethyl, 1,4-dithiane 2,5-diisocyanate, 1,4dithiane 2,5-diisocyanatomethyl, 1,4-dithiane 2,3-diisocyanatomethyl, 1,4-dithiane 2isocyanato methyl 5-isocyanato propyl, 1,3-dithiolane 4,5-diisocyanate, 1,3-dithiolane 4,5-diisocyanatomethyl, 1,3-dithiolane 2-methyl-4,5-diisocyanatomethyl, 1,3-dithiolane 2,2-diisocyanatoethyl, tetrahydrothiophene 2,5-diisocyanate, Sulfur content isocyanate compounds, such as tetrahydrothiophene 2,5-diisocyanatomethyl, tetrahydrothiophene 2,5-diisocyanatoethyl, and tetrahydrothiophene 3,4-diisocyanatomethyl.

The following can be mentioned as a polythiol compound.

(i) Methanedithiol, 1,2-ethanedithiol, 1,1-propanedithiol, 1,2-propanedithiol, 1,3propanedithiol, 2,2-propanedithiol, 1,6-HEKISANJI thiol, 1,2,3-propanetrithiol, Tetrakis (mercaptomethyl) methane, 1,1-cyclohexane JICHIORU, 1,2-cyclohexane JICHIORU, the 2,2-dimethylpropane- 1, 3-JICHIORU, 3,4-dimethoxy butane-1,2-JICHIORU, the 2methylcyclohexane 2, 3-JICHIORU, 1,1-bis(mercaptomethyl)cyclohexane, screw thiomalate (2-mercaptoethylester), 2, 3-dimercaptosuccinic acid (2-mercaptoethylester), 2,3-dimercapto 1-propanol (2-mercapto acetate), 2,3-dimercapto 1-propanol (3-mercapto acetate), A diethylene glycol screw (2-mercapto acetate), a diethylene glycol screw (3mercaptopropionate), 1,2-dimercapto propylmethyl ether, 2,3-dimercapto propylmethyl ether, 2,2-bis(mercaptomethyl)-1,3-propanedithiol, Bis(2-mercaptoethyl)ether, an ethylene glycol screw (2-mercapto acetate), An ethylene glycol screw (3mercaptopropionate), trimethylolpropanetris (2-mercapto acetate), Trimethylolpropanetris (3-mercaptopropionate), Aliphatic thiol, such as pentaerythritol

tetrakis (2-mercapto acetate), pentaerythritol tetrakis (3-mercaptopropionate), and 1,2bis(2-mercaptoethylthio)-3-mercaptopropane,

(ii) 1,2-dimercapto benzene, 1,3-dimercapto benzene, 1,4-dimercapto benzene, 1,2bis(mercaptomethyl)benzene, 1,3-bis(mercaptomethyl)benzene, 1,4bis(mercaptomethyl)benzene, 1,3-bis(mercaptoethyl)benzene, 1,4bis(mercaptoethyl)benzene, 1,2-bis(mercaptomethoxy)benzene, 1,3bis(mercaptomethoxy)benzene, 1,4-bis(mercaptomethoxy)benzene, 1,2-

bis(mercaptoethoxy)benzene, 1,3-bis(mercaptoethoxy)benzene, 1,4bis(mercaptoethoxy)benzene, 1,2,3-trimercapto benzene, 1,2,4-trimercapto benzene, 1,3,5-trimercapto benzene, 1,2,3-tris (mercaptomethyl) benzene, 1,2,4-tris (mercaptomethyl) benzene, 1,3,5-tris (mercaptomethyl) benzene, 1,2,3-tris (mercaptoethyl) benzene, 1,2,4-tris (mercaptoethyl) benzene, 1,3,5-tris (mercaptoethyl) benzene, 1,2,3-tris (mercaptomethoxy) benzene, 1,2,4-tris (mercaptomethoxy) benzene, 1,3,5-tris (mercaptomethoxy) benzene, 1,2,3-tris (mercaptoethoxy) benzene, 1,2,4-tris (mercaptoethoxy) benzene, 1,3,5-tris (mercaptoethoxy) benzene, 1,2,3,4tetramercaptobenzene, 1,2,3,5-tetramercaptobenzene, 1,2,4,5-tetramercaptobenzene, 1,2,3,4-tetrakis (mercaptomethyl) benzene, 1,2,3,5-tetrakis (mercaptomethyl) benzene, 1,2,4,5-tetrakis (mercaptomethyl) benzene, 1,2,3,4-tetrakis (mercaptoethyl) benzene, 1,2,3,5-tetrakis (mercaptoethyl) benzene, 1,2,4,5-tetrakis (mercaptoethyl) benzene, 1,2,3,4-tetrakis (mercaptoethyl) benzene, 1,2,3,5-tetrakis (mercaptomethoxy) benzene, 1,2,4,5-tetrakis (mercaptomethoxy) benzene, 1,2,3,4-tetrakis (mercaptoethoxy) benzene, 1,2,3,5-tetrakis (mercaptoethoxy) benzene, 1,2,4,5-tetrakis (mercaptoethoxy) benzene, 2,2'-dimercapto biphenyl, 4,4'-dimercapto biphenyl, 4,4'-dimercapto bibenzyl, 2,5-TORUENJI thiol, 3,4-TORUENJI thiol, 1, 4-NAFTA range thiol, 1, 5-NAFTA range thiol, 2,6-NAFTA range thiol, 2,7-NAFTA range thiol, the 2,4-dimethylbenzene 1, 3-JICHIORU, 4,5-dimethylbenzene 1,3-JICHIORU, 9,10-anthracenedimethanethiol, Aromatic thiol, such as 1,3-JI (p-methoxypheny) propane-2,2-JICHIORU, 1,3diphenylpropane-2,2-JICHIORU, phenylmethane-1,1-JICHIORU, and 2,4-JI (pmercaptophenyl) pentane,

- (iii) 2,5-dichlorobenzene 1,3-JICHIORU, the 1,3-JI (p-chlorophenyl) propane- 2, 2-JICHIORU, Halogenation aromatic thiol, such as chlorination objects, such as 3,4,5-bird bromine 1,2-dimercapto benzene and 2,3,4,6-Thet Laclos Lou 1,5-bis(mercaptomethyl)benzene, and a bromination object,
- (iv) 1,2-bis(mercaptomethyl thio)benzene, 1,3-bis(mercaptomethyl thio)benzene, 1,4-bis(mercaptomethyl thio)benzene, 1,2-bis(mercaptoethylthio)benzene, 1,3-bis(mercaptoethylthio)benzene, 1,4-bis(mercaptoethylthio)benzene, 1,2,3-tris (mercaptomethyl thio) benzene, 1,2,4-tris (mercaptomethyl thio) benzene, 1,3,5-tris (mercaptomethyl thio) benzene, 1,2,3-tris (mercaptoethylthio) benzene, 1,2,4-tris (mercaptoethylthio) benzene, 1,2,3,4-tetrakis (mercaptomethyl thio) benzene, 1,2,3,5-tetrakis (mercaptomethyl thio) benzene, 1,2,3,5-tetrakis (mercaptomethyl thio) benzene, 1,2,3,5-tetrakis (mercaptoethylthio) benzene, 1,2,3,5-tetrakis (mercaptoethylthio) benzene, 1,2,3,5-tetrakis (mercaptoethylthio) benzene, 1,2,4,5-tetrakis (mercaptoethylthio) benzene, etc., And aromatic thiol which contains a sulfur atom in addition to sulfhydryl groups, such as these nuclear alkylation things,
- (v) Bis(mercaptomethyl)sulfide, bis(mercaptoethyl)sulfide, Bis(mercaptopropyl)sulfide, bis(mercaptomethyl thio)methane, Bis(2-mercaptoethylthio)methane, bis(3-mercaptopropyl)methane, 1,2-bis(mercaptomethyl thio)ethane, 1,2-(2-mercaptoethylthio) ethane, 1,2-(3-mercaptopropyl) ethane, 1,3-bis(mercaptomethyl thio)propane, 1,3-bis(2-mercaptoethylthio)propane, 1,3-bis(3-mercaptopropylthio)propane, 1,2-bis(2-mercaptoethylthio)-3-mercaptopropane, 2-mercaptoethylthio- 1,3-propanedithiol, 1,2,3-tris (mercaptomethyl thio) propane, 1,2,3-tris (2-mercaptoethylthio) propane, 1,2,3-tris (3-mercaptopropylthio) propane, Tetrakis (mercaptomethyl thiomethyl) methane, tetrakis (2-mercaptoethyl thiomethyl) methane,

bis(2,3-dimercapto propyl)sulfide, 2,5-dimercapto 1,4-dithiane, bis(mercaptomethyl)disulfide, Bis(mercaptoethyl)disulfide, bis(mercaptopropyl)disulfide, etc., And ester of such thioglycolic acid and mercaptopropionic acid, A hydroxymethylsulfide screw (2-mercapto acetate), a hydroxymethylsulfide screw (3mercaptopropionate), A hydroxyethyl sulfide screw (2-mercapto acetate), a hydroxyethyl sulfide screw (3-mercaptopropionate), A hydroxypropyl sulfide screw (2-mercapto acetate), A hydroxypropyl sulfide screw (3-mercaptopropionate), A hydroxymethyl disulfide screw (2-mercapto acetate), A hydroxymethyl disulfide screw (3mercaptopropionate), A hydroxyethyl disulfide screw (2-mercapto acetate), A hydroxyethyl disulfide screw (3-mercaptopropionate), a hydroxypropyl disulfide screw (2-mercapto acetate), a hydroxypropyl disulfide screw (3-mercaptopropionate), 2mercaptoethyl ether screw (2-mercapto acetate), 2-mercaptoethyl ether screw (3mercaptopropionate), A 1,4-dithiane 2,5-diol screw (2-mercapto acetate), A 1,4-dithiane 2,5-diol screw (3-mercaptopropionate), Screw thioglycolate (2-mercaptoethylester), screw thiodipropionate (2-mercaptoethylester), A 4,4'-thiodibutylacid screw (2mercaptoethylester), Screw dithiodiglycolate (2-mercaptoethylester), a dithio dipropionic acid screw (2-mercaptoethylester), A 4,4'-dithio dibutylacid screw (2mercaptoethylester), Screw thiodiglycolate (2, 3-dimercapto propyl ester), Screw thiodipropionate (2, 3-dimercapto propyl ester), Screw dithiodiglycolate (2,3-dimercapto propyl ester), dithio dipropionic acid (2,3-dimercapto propyl ester), the 4-mercaptomethyl 3,6-dithia octane- 1, 8-JICHIORU, Bis(mercaptomethyl)-3,6,9-trithia 1,11undecanedithiol. The aliphatic thiol which contains a sulfur atom in addition to sulfhydryl groups, such as bis(1,3-dimercapto 2-propyl)sulfide, (vi) 3,4-thio FENJI thiol, tetrahydrothiophene 2,5-dimercaptomethyl, The heterocyclic compound which contains a sulfur atom in addition to sulfhydryl groups, such as 2,5-dimercapto 1,3,4-thiadiazole, 2.5-dimercapto 1.4-dithiane, and 2.5-dimercaptomethyl 1.4-dithiane. The following are mentioned as a polyhydroxy compound. (i) Ethylene glycol, diethylene glycol, propylene glycol, Dipropylene glycol, butylene glycol, neopentyl glycol, Glycerol, trimethylolethane, trimethylolpropane, butanetriol, A 1,2-methyl GURUKO side, pentaerythritol, dipentaerythritol, Tripentaerythritol, triethylene glycol, polyethylene glycol, tris (2-hydroxyethyl) isocyanurate, cyclobutanediol, cyclopentane diol, cyclohexanediol, cycloheptanediol, cyclooctanediol, bicyclo 4, [3, 0] - Nonanediol, dicyclohexanediol, tricyclo [5,3,1, 1] Spiro [dodecanediol, [3, 4] Aliphatic series polyols, such as octanediol and butyl cyclo hexandiol, (ii) Dihydroxy naphthalene, trihydroxy naphthalene, tetrahydroxy naphthalene, Aromatic polyols, such as dihydroxybenzene, benzenetriol, trihydroxy phenanthrene, bisphenol A, the bisphenol F, a KISHIRIREN glycol, and tetra bromine bisphenol A, (iii) The addition reaction product of the polyhydroxy compound of the above-mentioned (i) or (ii), and alkylene oxide, such as ethyleneoxide and propylene oxide, (iv) bis- [4-(hydroxy ethoxy) phenyl] Sulfide, bis-[4-(2-hydroxy propoxy) phenyl] Sulfide, bis-[4-(2,3-dihydroxy propoxy) phenyl] Sulfide, bis- [4-(4-hydroxy cyclo hexyloxy) phenyl] Sulfide, bis-[2-methyl-4-(hydroxy ethoxy)-6-buthylphenyl] The compound in which ethylene oxide and/or propylene oxide of an average of three molecules [per hydroxyl group ] or less were added to sulfide and these compounds, Di-(2-hydroxyethyl)sulfide, 1,2-bis-(2-hydroxyethyl mercapto) ethane, Bis(2-hydroxyethyl)disulfide, 1,4-dithiane 2,5-diol, Bis(2,3-dihydroxy propyl)sulfide, tetrakis (4-hydroxy-2-thiabutyl) methane,

Bis(4-hydroxyphenyl)sulfone (trade name bisphenol S), The polyol containing sulfur atoms, such as the tetrabromo bisphenol S, the tetramethyl bisphenol S, 4,4'-thiobis-(6tert-butyl-3-methylphenol), and 1,3-bis(2-hydroxyethyl thioethyl)-cyclohexane. What is used as a lens substrate is conventionally known among poly(thio) urethane resin, and, [this] [as a concrete example of a publicly known publication which is indicating ] For example, JP,S58-127914,A, JP,S57-136601,A, JP,H01-163012,A, JP,H03-236386,A, JP,H03-281312,A, JP,H04-159275,A, JP,H05-148340,A, JP,H06-065193, A, JP, H06-256459, A, JP, H06-313801, A, JP, H06-192250, A, JP, H07-063902, A, JP,H07-104101,A, JP,H07-118263,A, JP,H07-118390,A, JP,H07-316250,A, JP,S60-199016, A, JP, S60-217229, A, JP, S62-236818, A, JP, S62-255901, A, JP, S62-267316, A, JP,S63-130615,A, JP,S63-130614,A, JP,S63-046213,A, JP,S63-245421,A, JP,S63-265201, A, JP, H01-090167, A, JP, H01-090168, A, JP, H01-090169, A, JP, H01-090170, A, JP,H01-096208,A, JP,H01-152019,A, JP,H01-045611,A, JP,H01-213601,A, JP,H01-026622, A, JP, H01-054021, A, JP, H01-311118, A, JP, H01-295201, A, JP, H01-302202, A, JP,H02-153302,A, JP,H01-295202,A, JP,H02-802,A, JP,H02-036216,A, JP,H02-058517, A, JP, H02-167330, A, JP, H02-270859, A, JP, H03-84031, A, JP, H03-084021, A, JP,H03-124722,A, JP,H04-78801,A, JP,H04-117353,A, JP,H04-117354,A, JP,H04-256558, A, JP, H05-78441, A, JP, H05-273401, A, JP, H05-093801, A, JP, H05-080201, A, JP,H05-297201,A, JP,H05-320301,A, JP,H05-208950,A, JP,H06-072989,A, JP,H06-256342, A, JP, H06-122748, A, JP, H07-165859, A, JP, H07-118357, A, JP, H07-242722, A, JP,H07-247335,A, JP,H07-252341,A, JP,H08-73732,A, JP,H08-092345,A, JP,H07-228659, A. JP, H08-3267, A. JP, H07-252207, A. JP, H07-324118, A. JP, H09-208651, A. etc. are mentioned. It cannot be overemphasized that the polyisocyanate compound, polythiol compound, and polyhydroxy compound which are indicated by these gazettes correspond to the raw material monomer for manufacturing poly(thio) urethane resin as used in the field of this invention.

The copolymer to which make the homopolymer of diethylene glycol bisallyl carbonate and diethylene glycol bisallyl carbonate, and a copolymerizable monomer come to react as resin which makes diethylene glycol bisallyl carbonate a principal component is mentioned.

[ as diethylene glycol bisallyl carbonate and a copolymerizable monomer ] Methyl methacrylate, ethyl methacrylate, methacrylic acid n-butyl, Methacrylic acid ethylhexyl, benzyl methacrylate, phenyl methacrylate, Monofunctional methacrylic acid ester, such as cyclohexyl methacrylate, methacrylic acid isobornyl, and methacrylic acid adamanthyl, is mentioned, and, [ as polyfunctional methacrylic acid ester ] Ethylene glycol dimethacrylate, diethylene glycol dimethacrylate, Triethylene glycol dimethacrylate, tripropylene glycol dimethacrylate, 1,4-butanediol dimethacrylate, 1,6hexanedioldimethacrylate, trimethylolpropanetrimethacrylate, pentaerythritol trimethacrylate, glycerol dimethacrylate, a 2,2-screw [4-(meta-KURIROKISHI) phenyl] Propane, a 2,2-screw [4-(meta-KURIROKISHI ethoxy) phenyl] Propane etc. are mentioned. Methyl acrylate, ethyl acrylate, acrylic acid n-butyl, Acrylic acid ethylhexyl, cyclohexyl acrylate, benzyl acrylate, Phenyl acrylate, acrylic acid isobornyl, ethylene glycol diacrylate, triethylene glycol diacrylate, 1,6-hexanediol diacrylate, trimethylolpropane triacrylate, pentaerythritol bird acrylate, a 2,2-screw [4-(acryloxy) phenyl] Propane, a 2,2-screw [4-(acryloxy ethoxy) phenyl] To acrylic ester, such as propane, and a pan, styrene, methylstyrene, Dimethylstyrene, KURORU styrene, dichloro styrene, bromine styrene, Nuclear substitution styrene, such as p-KURORU methylstyrene and divinylbenzene, alpha-methylstyrene, acrylonitrile, methacrylonitrile, maleic anhydride, N-substitution maleimide, diallyl phthalate, diallyl isophthalate, diaryl terephthalate, etc. are mentioned.

The copolymer of diethylene glycol bisallyl carbonate and other monomers is known, and what was indicated in JP,S54-41965,A, JP,S51-125487,A, a special playback common No. 503809 [ 01 to ] gazette, etc. is mentioned as the example.

The resin obtained from an epithio group content compound uses as a raw material the monomer mixture containing the monomer which has an epithio group, or this monomer, and refers to the resin which polymerizes this, and the following are mentioned as an example of the monomer which has an epithio group.

- (i) 1,3 and 1,4-bis(beta-epithiopropyl-thio)cyclohexane, 1,3 and 1,4-bis(beta-epithiopropyl thiomethyl)cyclohexane, a screw [4-(beta-epithiopropyl-thio) cyclohexyl] Methane, a 2,2-screw [4-(beta-epithiopropyl-thio) cyclohexyl] Propane, a screw [4-(beta-epithiopropyl-thio) cyclohexyl] The episulfide compound which has alicycle group skeletons, such as sulfide,
- (ii) 1,3 and 1,4-bis(beta-epithiopropyl-thio)benzene, 1,3 and 1,4-bis(beta-epithiopropyl thiomethyl)benzene, a screw [4-(beta-epithiopropyl-thio) phenyl] Methane, a 2,2-screw [4-(beta-epithiopropyl-thio) phenyl] Propane, a screw [4-(beta-epithiopropyl-thio) phenyl] Sulfide, a screw [4-(beta-epithiopropyl-thio) phenyl] The episulfide compound which has aromatic skeletons, such as sulfine and 4,4-bis(beta-epithiopropyl-thio)biphenyl,
- (iii) 2,5-bis(beta-epithiopropyl thiomethyl)-1,4-dithiane, 2,5-bis(beta-epithiopropyl-thio ethyl thiomethyl)-1,4-dithiane, The episulfide compound which has dithiane ring skeletons, such as 2,5-bis(beta-epithiopropyl-thio ethyl)-1,4-dithiane and 2,3,5-bird (beta-epithiopropyl-thio ethyl)-1,4-dithiane,
- (iv) 2-(2-beta-epithiopropyl-thio ethylthio)-1,3-bis(beta-epithiopropyl-thio)propane, a 1,2-screw [(2-beta-epithiopropyl-thio ethyl) Thio] The epithio compound which has aliphatic series skeletons, such as-3-(beta-epithiopropyl-thio) propane, tetrakis (beta-epithiopropyl thiomethyl) methane, 1,1,1-tris (beta-epithiopropyl thiomethyl) propane, and bis-(beta-epitiopropyl)surfide.

What is used as a plastic lens substrate among the resin obtained from an epithio group content compound is known conventionally, and, [ as the example ] JP,H09-071580,A, JP,H09-110979,A, JP,H09-255781,A, JP,H03-081320,A, What was indicated in JP,H11-140070,A, JP,H11-183702,A, JP,H11-189592,A, JP,H11-180977,A, a special playback common No. 810575 [ 01 to ] gazette, etc. is mentioned.

Can illustrate to intramolecular the radical polymer which has urethane (thio) structure as other examples, and to it specifically, . [ by making the straight-chain-shape alkane compound of the carbon numbers 3-6 which have at least two sulfhydryl groups in a molecule, and the compound which has at least one isocyanate group and at least one acrylyl group (meta) in a molecule react ] The radical polymer using the monomer obtained can be illustrated. An acrylyl group (meta) means both an acrylyl group and a methacryloyl group.

[ as an example of the straight-chain-shape alkane compound of the carbon numbers 3-6 which have at least two sulfhydryl groups in the molecule which is one of the raw materials of a radical polymerization nature compound with the above thio urethane

bonds ] 1,2,3-trimercapto propane, 1,2,3-trimercapto butane, 1,2,4-trimercapto butane, 1,2,3,4-tetramercaptobutane, 1,2,3-trimercapto pentane, 1,2,4-trimercapto pentane, 1,2,3-trimercapto hexane, 1,2,4-trimercapto hexane, 1,2,5-trimercapto hexane, 2,3,4-trimercapto hexane, 2,3,5-trimercapto hexane, 3,4,5-trimercapto hexane, 1,2,3,4-tetramercaptohexane, Although 1,2,3,5-tetramercaptohexane, 1,2,4,5-tetramercaptohexane, 2,3,4,5-tetramercaptohexane, and 1,2,3,4,5-pentamercaptohexane can be mentioned, Points, such as performance of an optical material and ease of acquisition, to the 1,2,3-trimercapto propane obtained especially in these is preferred.

[ as an example of the compound which is another raw material and which has one isocyanate group and at least one acrylyl group (meta) in a molecule at least ] Although an acryloyl isocyanate, a methacryloyl isocyanate, 2-isocyanato ethyl acrylate, 2-isocyanato ethyl methacrylate, 2-isocyanato propyl methacrylate, etc. are mentioned, In these, points, such as performance of an optical material and ease of acquisition, to 2-isocyanato ethyl methacrylate obtained especially is preferred. Although what was illustrated in the top has one isocyanate group and one acrylyl group (meta), it may have two or more isocyanate groups, and may have two or more acrylyl groups (meta).

When using the above-mentioned organic inorganic composite as an optical material, in order to improve the physical properties suitably, When the organic monomer in which a radical polymerization is possible is used, for example in addition to said polymerization nature compound, as copolymerizable [ having a radical polymerization group ] a radical polymerization nature compound as the above-mentioned compound -- one sort -- or two or more sorts being included and as this radical polymerization nature compound, Specifically Methyl (meta) acrylate, ethyl (meta) acrylate, Propyl (meta) acrylate, butyl (meta) acrylate, 2-ethylhexyl (meta) acrylate, Benzyl (meta) acrylate, butoxy ethyl (meta) acrylate, Cyclohexyl (meta) acrylate, 2-hydroxyethyl (meta) acrylate, Glycidyl (meta) acrylate, phenoxyethyl (meta) acrylate, Ethylene glycol di(metha)acrylate, diethylene GURIKORUJI (meta) acrylate, Triethylene glycol di(metha)acrylate, tetraethylene jig RIKORUJI (meta) acrylate, poly ethylene glycol di(metha)acrylate, neopentyl KURIKORUJI (meta) acrylate, Ethylene glycol screw glycidyl (meta) acrylate, bisphenol A di(meth)acrylate, 2,2-bis(4-(meta) acryloxy diethoxyphenyl)propane, Trimethylolpropane bird (meta) acrylate, GURISERORUJI (meta) acrylate, Diallyl phthalate, diaryl terephthalate, diallyl isophthalate, Diaryl carbonate, diethylene glycol bisallyl carbonate, Styrene, chloro styrene, methylstyrene, bromostyrene, dibromo styrene, 2,5-bis(2-cheer 3-butenyl)-1,4-dithiane, 2,5-bis(meta)(acryloyl thiomethyl)-1,4dithiane, etc. are mentioned, and 2,5-bis(2-cheer 3-butenyl)-1,4-dithiane is mentioned especially preferably. The above-mentioned (meta) acrylate means both acrylate and methacrylate, and an acryloxy (meta) group means both an acryloxy group and a meta-KURIROKISHI group.

When a polymerization reaction is an organic monomer in which radical or cationic polymerization of an organic monomer is possible, A publicly known radical or cationic initiator, [ an organic monomer ] In the case of polyaddition or the organic monomer in which polycondensation is possible, a triethylene diamine, Hexamethylenetetramine, N,N-dimethyl octylamine, N,N,N',N'-tetramethyl 1,6-diaminohexane, Amine compounds, such as 4,4'-trimethylene screw (1-methyl piperidine), 1, and 8-diazabicyclo [5, 4, 0]-7-

undecene, Or dimethyltin dichloride, a dimethyltin screw (isooctylthioglycolate), Dibutyltin dichloride, dibutyltin dilaurate, dibutyltin maleate, Dibutyltin maleate polymer, dibutyl SUZUJI triricinolate, a dibutyltin screw (dodecylmercaptide), A dibutyltin screw (isooctylthioglycolate), dioctyltin dichloride, Dioctyltin maleate, dioctyltin maleate polymer, a dioctyltin screw (butyl maleate), dioctyl SUZUJI laurate, dioctyl SUZUJI triricinolate, dioctyltin dioleate, Dioctyl SUZUJI (6-hydroxy) caproate, a dioctyltin screw (isooctylthioglycolate), It polymerizes by adding organometallic compounds, such as didodecyl SUZUJI triricinolate, copper oleate, acetylacetone \*\*\*\*, acetylacetone iron-oxide, iron naphthenate, iron lactate, ferric citrate, iron gluconate, potassium octanoate, and 2-ethylhexyl titanate. Among said polyaddition or the catalyst of a polycondensation reaction, especially, dibutyltin dichloride and dibutyltin dilaurate are preferred, and these catalysts may be used independently and may be used combining two or more sorts.

When performing an optical radical polymerization, for reactant improvement Benzophenone, 4,4-diethylamino benzophenone, 1-hydroxy cyclohexyl phenyl ketone, p-dimethylamino isoamyl benzoate, 4-dimethylamino methyl benzoate, Benzoin, benzoin ethyl ether, benzoin isobutyl ether, Publicly known sensitizers, such as benzoin-iso-propyl-ether, 2,2-diethoxy acetophenone, methyl o-benzoylbenzoate, and 2-hydroxy-2-methyl-1-phenylpropane-1-ON and acyl phosphine oxide, can also be added. Said polymerization reaction can perform either solution polymerization or bulk polymerization, and can polymerize the mixture of an organic ingredient and a mineral constituent by performing heating or light irradiation.

As the manufacturing method of organic inorganic composite,

- (1) A method which is mixed with the inside of an organic solvent, or bulk, and carries out the fabrication of the dispersoid which has the metal-oxygen bond prepared from organic polymer, metal alkoxide, etc.,
- (2) How to prepare the dispersoid which has a metal-oxygen bond from metal alkoxide etc. among an organic solvent, add an organic monomer, and perform and carry out the fabrication of solution polymerization or the bulk polymerization,
- (3) How to mix an organic monomer with metal alkoxide etc. among an organic solvent, prepare the mixture of the dispersoid which hydrolyzes by adding water and has an organic monomer and a metal-oxygen bond, and perform and carry out the fabrication of solution polymerization or the bulk polymerization,
- (4) How to mix metal alkoxide etc. with organic polymer in an organic solvent, add water, hydrolyze, and carry out a fabrication,
- (5) It can do, although the method of carrying out dropping mixing and carrying out the fabrication of the organic solvent which contains organic polymer in the organic solvent containing the dispersoid which has the metal-oxygen bond prepared from metal alkoxide etc., etc. are illustrated, and the method of of (2) or (3) is especially preferred. In the method of (3), when using a polycondensation thing as organic polymer, it is preferred to carry out [ which prepared the dispersoid in which an unstable monomer has a metal-oxygen bond to water ] adding after mixing.

Since the organic inorganic composite of this invention has a high refractive index and high visible light transmittance, using as an optical material is preferred. In order to improve extinction characteristics, to improve weatherability for an ultraviolet ray absorbent, a pigment, a pigment, etc. and to improve molding workability for an

antioxidant, a color protection agent, etc., a release agent etc. can be suitably added to this optical material by request. Here, as an ultraviolet ray absorbent, a benzotriazol system, a benzophenone series, a salicylic acid system, etc. are mentioned, and an anthraquinone system, azo, etc. are mentioned as a pigment or a pigment, for example. As an antioxidant or a color protection agent, a mono- phenol system, a bisphenol system, a polymer type phenol system, a sulfur system, a phosphorus system, etc. are mentioned, and a fluorochemical surfactant, a silicone series surface active agent, alkyl acid phosphate, a higher fatty acid, etc. are mentioned as a release agent, for example. The dispersoid which has said oxygen-metallic bond about the manufacturing method of the optical material of this invention, for example, If it is a monomer of radical polymerization nature, for example, [ the homogeneous mixture containing said organic monomer, this monomer, a copolymerizable monomer and an additive, or a catalyst 1 It pours in into the mold which combined the mold of glass [ which penetrates the publicly known casting polymerizing method, i.e., ultraviolet radiation, ], or the product made of resin, and the gasket made of resin, and ultraviolet radiation is irradiated with and stiffened, and it will be made to heat and harden if it is polyaddition and a polycondensation nature monomer. Under the present circumstances, in order to make extraction of resin after shaping easy, mold release treatment of the mold may be carried out beforehand, or a release agent may be made to contain in said homogeneous-mixing liquid. Furthermore, after UV irradiation, in order to complete a polymerization or to make the stress generated inside material ease, heating is also performed preferably. Although the cooking temperature and time in this case change with UV irradiation amounts of energy etc., generally they are 30-150 \*\* and 0.2 to 24 hours, respectively. As for initial temperature, in the casting polymerization by heating, it is preferred for the range of low-temperature to be comparatively preferred, to carry out temperature rising to 5-40 \*\* gradually over 10 to 70 hours, and to make it 100-130 \*\* high temperature, for example. About the optical material obtained by the above (1) which manufacture of organic polymer has already ended, or a manufacturing method as shown in (4), it can fabricate by casting a solution with a mold. Thus, the optical material of obtained this invention usually has a refractive index of 1.60 or more. Although the optical material of this invention can be easily dyed in water or an organic solvent using the usual disperse dye, in order to dye easily further in this case, Carrier may be added or it may heat. This invention is what also provides the optical goods which consist of an optical material produced by doing in this way again, Although there is no restriction in particular as these optical goods, for example, optical plastic lenses including a glasses lens, prism, an optical fiber, the substrate for recording media, a filter and also a glass, a flower vase, etc. can be mentioned, In these, it is used suitably for an optical plastic lens, especially a glasses lens.

Without carrying out a casting polymerization, the optical material of this invention can be applied to the surfaces, such as a lens or glass, can be stiffened by operating light irradiation etc. if needed, and can also be used as a raw material of the hard court film which protects the surface, and the multilayer coating which prevents a reflection. Although a coating method in particular is not limited, any methods, such as a dip coat, a spin coat, a flow coat, roller coating, and brush coating, are employable. The best form for inventing

Although this invention is explained still in detail using an embodiment below, this

invention is not limited to an embodiment.

#### Embodiment 1

7.87 g (27.7mmol) of titanium tetraisopropoxide (Nippon Soda [ Co., Ltd. ] make A-1: 99.9% of purity, 28 weight % of titanium oxide conversion concentration), [ in 4 mouth flask ] It dissolved in tetrahydrofuran, and after carrying out nitrogen gas substitution, it cooled by the methanol bath (about-74 \*\*) which added dry ice. After cooling about 20 minutes, it added agitating the distilled water (0.8g:44.4mmol as distilled water) diluted with tetrahydrofuran. At this time, the gross weight of tetrahydrofuran could be 32.12 g. The amount of additive water at this time is H<sub>2</sub>O/Ti=1.6 molar ratio. When it returned to the room temperature gradually after that, the tetrahydrofuran solution containing the hydrolyzate of the titanium isopropoxide of light yellow transparence was obtained. The appearance of the tetrahydrofuran solution obtained at this time was shown in the 1st table. The visible light transmittance (550 nm) of this solution was 87%. The UV characteristics of the solution prepared as mentioned above were shown in Fig. 1. The UV characteristics of titanium tetraisopropoxide were also written together to Fig. 1. If both are compared, low-temperature hydrolyzate is excellent in UV cut nature as compared with titanium tetraisopropoxide.

It turns out that Ti-O-Ti binding is growing.

## Comparative example 1

In Embodiment 1, it carried out like Embodiment 1 except the weight of the distilled water to add having been 1.0 g (55.6mmol). The appearance of the tetrahydrofuran solution obtained at this time was shown in the 1st table.

# Comparative example 2

In Embodiment 1, it carried out like Embodiment 1 except the weight of the distilled water to add having been 1.2 g (66.7mmol). The appearance of the tetrahydrofuran solution obtained at this time was shown in the 1st table.

### Embodiment 2

By the rotating evaporator, the vacuum concentration of the tetrahydrofuran solution obtained in Embodiment 1 was carried out with the degree of bath temperature of 50 \*\*, and the transparent viscosity fluid was obtained with the light yellow of 40.2 weight % of titanium oxide conversion concentration. the place which added the tetrahydrofuran solvent to this fluid -- it remelted.

	蒸留水/チタンテトライソ	TiO <sub>2</sub> 換算重量	- 7 4 ℃での	室温での外観
	プロポキシド(モル比)	濃度 (%)	外観	
実施例 1	1.6	5.4	淡黄色透明	淡黄色透明
実施例2	1.6	40.2	_	淡黄色透明
比較例I	2. 0	5.4	淡黄色透明	白濁ゲル状
比較例2	2.4	5.4	淡黄色透明	白濁ゲル状

第1表

#### Embodiment 3

12.4 g of titanium tetraisopropoxide (Nippon Soda [ Co., Ltd. ] make A-1: 99% of purity, 28.2 weight % of titanium oxide conversion concentration) was cooled at -80 \*\* all over ethanol / liquid nitrogen bus, after dissolving in 45.0 g of toluene and carrying out nitrogen gas substitution in 4 mouth flask. Independently, where the ion exchange water 1.26g (H<sub>2</sub>O/Ti=1.6 molar ratio) is cooled at -80--70 \*\* after mixing to 11.3 g of isopropanol, it was dropped agitating into the above-mentioned 4 mouth flask, and hydrolyzed. During dropping, the solution temperature in a flask was maintained at -80--70 \*\*. Temperature rising was carried out agitating to a room temperature after churning after the end of dropping cooling for 30 minutes, and sol of 5 weight % of water-white titanium oxide conversion concentration was obtained. The visible light transmittance (550 nm) of this solution was 85%.

# Embodiment 4

By the rotating evaporator, the solution obtained in Embodiment 3 was condensed with the degree of bath temperature of 50 \*\*, and the viscosity fluid of 54.3 weight % of titanium oxide conversion concentration was obtained. the place which added the toluene solvent to this fluid -- it remelted.

#### Embodiment 5

10.8 g of zirconium tetra n butoxide (TBZR by Nippon Soda Co., Ltd.: 87% of purity, 32.2 weight % of zirconium oxide conversion concentration) was cooled at -80 \*\* all over ethanol / liquid nitrogen bus, after dissolving in the toluene solution 46.9g and carrying out nitrogen gas substitution in 4 mouth flask. Independently, where the ion exchange water 0.812g (H<sub>2</sub>O/Zr=1.6 molar ratio) is cooled at -80--70 \*\* after mixing at the 2-butanol 7.30g, it was dropped agitating into the above-mentioned 4 mouth flask, and hydrolyzed. During dropping, the solution temperature in a flask was maintained at -80--70 \*\*. Temperature rising was carried out agitating to a room temperature after churning after the end of dropping cooling for 30 minutes, and sol of 5 weight % of water-white zirconium oxide conversion concentration was obtained. The visible light transmittance (550 nm) of this solution was 88%.

#### Embodiment 6

By the rotating evaporator, the solution obtained in Embodiment 5 was condensed with the degree of bath temperature of 50 \*\*, and the viscosity fluid of 43 weight % of zirconium oxide conversion concentration was obtained. the place which added the toluene solvent to this fluid -- it remelted.

#### Embodiment 7

9.12 g of tantalumpentaethoxide (Kojundo Chemical Laboratory [ Co., Ltd. ] make: 99% of purity, 54.4 weight % of tantalum oxide conversion concentration), [ in 4 mouth flask ] It dissolved in 42.1 g of toluene, and the mixed solution of 42.1 g of ethanol, and after carrying out nitrogen gas substitution, it cooled at -80 \*\* all over ethanol / liquid nitrogen bus. Independently, where the ion exchange water 0.652g (H<sub>2</sub>O/Ta=1.6 molar ratio) is cooled at -80--70 \*\* after mixing to the mixed solvent of 2.96 g of toluene, and 2.96 g of ethanol, it was dropped agitating into the above-mentioned 4 mouth flask, and hydrolyzed. During dropping, the solution temperature in a flask was maintained at -80--70 \*\*. Temperature rising was carried out agitating to a room temperature after churning after the end of dropping cooling for 30 minutes, and sol of 5 weight % of water-white tantalum oxide conversion concentration was obtained. The visible light transmittance

(550 nm) of this solution was 88%.

**Embodiment 8** 

By the rotating evaporator, the solution obtained in Embodiment 7 was condensed with the degree of bath temperature of 50 \*\*, and the viscosity fluid of 64.5 weight % of tantalum oxide conversion concentration was obtained. the place which added the toluene solvent to this fluid -- it remelted.

Embodiment 9

Indium bird isopropoxide (Kojundo Chemical Laboratory [ Co., Ltd. ] make:) [ 99% of purity ] 47.4 weight % of indium oxide conversion concentration of 5.00 g, a tin tetra isopropoxide isopropanol addition product (the product made from AZUMAKKUSU:) [ 99% of purity ] The 2 tin-oxide conversion 42.6 weight % concentration of 0.79 g was cooled at -80 \*\* all over ethanol / liquid nitrogen bus, after dissolving in the toluene solution 44.5g and carrying out nitrogen gas substitution in 4 mouth flask. Independently, where the ion exchange water 0.370g (H<sub>2</sub>O/(In+Sn) =1.08 molar ratio) is cooled at -80-70 \*\* after mixing to 3.33 g of isopropanol, it was dropped agitating into the abovementioned 4 mouth flask, and hydrolyzed. During dropping, the solution temperature in a flask was maintained at -80--70 \*\*. carrying out temperature rising, agitating to a room temperature after churning after the end of dropping cooling for 30 minutes -- yellow -- transparent indium oxide of 5 weight % of metal oxide (In<sub>2</sub>O<sub>3</sub>, SnO<sub>2</sub>) conversion concentration and mixed sol of tin oxide were obtained. The visible light transmittance (550 nm) of this solution was 75%.

Embodiment 10

By the rotating evaporator, the solution obtained in Embodiment 9 was condensed with the degree of bath temperature of 50 \*\*, and the concentrate of 70 weight % of metal oxide conversion concentration was obtained. the place which added the toluene solvent to this concentrate -- it remelted.

Embodiment 11

66.84 g of partial hydrolysate (Nippon Soda Co., Ltd. make A-10) of titanium tetraisopropoxide was cooled at -80 \*\* all over ethanol / liquid nitrogen bus, after dissolving in 402.74 g of toluene and carrying out nitrogen gas substitution in 4 mouth flask. Where the ion exchange water 3.38g is independently cooled at -80--70 \*\* after mixing to 30.42 g of isopropanol, it was dropped agitating into the above-mentioned 4 mouth flask, and hydrolyzed. During dropping, the solution temperature in a flask was maintained at -80--70 \*\*. Temperature rising was carried out agitating to a room temperature after churning after the end of dropping cooling for 30 minutes, and sol of 5 weight % of water-white titanium oxide conversion concentration was obtained. The visible light transmittance (550 nm) of this solution was 92%.

Embodiment 12

By the rotating evaporator, the solution obtained in Embodiment 11 was condensed with the degree of bath temperature of 50 \*\*, and the viscous liquid object of 52.3 weight % of titanium oxide conversion concentration was acquired. It remelted by adding a toluene solvent to this fluid.

Embodiment 13

[ the tetrahydrofuran solution 3.0g containing the hydrolyzate of the titanium isopropoxide prepared in Embodiment 1 ] It cools by the methanol bath (abbreviation . 74 \*\*) which added dry ice, Dropping and mixing of were done agitating to the

tetrahydrofuran solution containing 4.2 g of 2,5-screw mercapto-1,4-dithiane (BMMD), and 4.6 g of 2,5-(screw isocyanate methyl)-1,4-dithiane (BIMD). After mixing, after returning to a room temperature gradually, 0.06 g of dilauric acid dibutyltin (made by Nacalai Tesque, Inc.) was added and agitated. Then, solvent distilling off and degassing were performed. After pouring this into glass dice and sealing a mold, from a room temperature to 120 \*\*, temperature rising is carried out gradually and the heating polymerization was carried out for 24 hours, and it cooled to the room temperature after that, and took out from the die, and the transparent massive object was acquired. It asked for the refractive index of the massive object acquired at this time with the Abbe refractive-index meter. The value of the refractive index was shown in the 2nd table. Embodiment 14

Except using 1.5g of tetrahydrofuran solutions containing the hydrolyzate of the titanium isopropoxide prepared in Embodiment 1, it carried out like Embodiment 13, and the result was summarized in the 2nd table and shown.

# Comparative example 3

It carried out like Embodiment 13 except not using the tetrahydrofuran solution which contains the hydrolyzate of titanium isopropoxide in Embodiment 13. The refractive index of the massive object acquired at this time was shown in the 2nd table. 第 2 表

加水分解物 BMMD BIMD 屈折率 溶液 (g) (g) (g) 実施例1 0 3 3. 4. 2 6 1. 6 5 6 実施例14 5 2 1. 4. 4. 6 1. 640 0 2 比較例3 0. 4. 6 4. 1. 6 3 3

#### Embodiment 15

the silicon wafer. It is Litho Tech Japan about the reflection spectrum of this thin film. Make FILMETRICS F It measures using series model F20, By piling up that spectrum with the simulation spectrum acquired when an optical constant is changed, the thickness of this thin film and the refractive index at 633 nm were measured. The thickness and the refractive index at this time are shown in the 3rd table.

### Embodiment 16

Except having prepared the toluene solution which uses toluene instead of tetrahydrofuran and contains the hydrolyzate of titanium tetraisopropoxide by the same method as Embodiment 1, it carried out like Embodiment 15 and the water-white solution was obtained.

Thickness and a refractive index were measured for this transparent solution by the same method as Embodiment 15. A result is shown in the 3rd table.

第3表

	膜厚 (nm)	屈折率
実施例15	1 3 0	1.87
実施例16	250	1.88

#### Embodiment 17

Except having prepared the solution which replaces with tetrahydrofuran as a diluent of distilled water, and contains the hydrolyzate of titanium tetraisopropoxide by the same method as Embodiment 1 using isopropanol, it carried out like Embodiment 15 and the transparent solution was obtained. The titanium oxide conversion concentration of this solution was 58.2-mol %.

Thickness and a refractive index were measured for this transparent solution by the same method as Embodiment 15. As a result, the refractive index of thickness was 1.87 in 134 nm.

### **Embodiment 18**

Membranes were formed on the glass substrate by bar coater (No.5), the tetrahydrofuran solution prepared like Embodiment 1 was dried for 30 minutes at 150 \*\*, and 0.1-micrometer-thick titanium oxide membrane was obtained. The contact angle over the water of this film was 42 degrees. The place and contact angle which irradiated with the near-ultraviolet light with the black light of 15W for 1 hour fell to this film to 12 degrees, and showed good hydrophilicity to it. Since the isopropoxy group which remains by UV irradiation \*\*\*\*ed, it thinks.

### Embodiment 19

The solution obtained in Embodiment 11 was formed on the glass substrate by bar coater (No.5), it dried for 30 minutes at 150 \*\*, and 0.1-micrometer-thick titanium oxide membrane was obtained. The contact angle over the water of this film was 28 degrees. When irradiating this film with the 2mW[/cm] <sup>2</sup> near-ultraviolet light with the black light of 15W for 1 hour, the contact angle fell to 3 degrees and showed good hydrophilicity. In the ultimate analysis of the thin film by a XPS device (Quantum2000) (product made from ULVAC Phi), the carbon element concentration (formula I) in the film after UV

### 炭素元素濃度×100

## 炭素元素濃度+チタン元素濃度+酸素元素濃度

#### Embodiment 20

the solution 270g and photocatalyst titania which were obtained in Embodiment 11 -- the solution which mixed the solution 30g which diluted sol (TKS-251 by TAYCA CORP.) so that it might become 5 weight % of solid content with toluene was prepared. On the glass substrate and the metallic Al base, this solution was formed by dip, and drying at 100 \*\* and a 0.3-micrometer-thick film were prepared.

In order to investigate the photocatalyst activity of this film, it irradiated with the ultraviolet radiation of the hardness of 2 mW/cm<sup>2</sup> with the black light after spreading so that it might become about 0.1 mg/cm<sup>2</sup> about salad oil on a film. A result is shown in the 4th table. Salad oil was disassembled for a short time, and high photocatalyst activity was shown.

第4表

試料	基板	外観	密着性	サラダオイル分解率(注)
2 0 - 1	ガラス	透明	良好	70%
20 - 2	金属アルミ	透明	良好	80%

(注) BLB 照射時間72時間

### Embodiment 21

Membranes were formed by bar coater (No.5) on the glass substrate which carried out the coat of the golden electrode, the toluene solution adjusted like Embodiment 7 was dried for 30 minutes at 150 \*\*, and the 0.1-micrometer-thick tantalum oxide film was obtained. The golden electrode was attached by the sputtering technique on this film, and membranous permittivity was measured. Membranous permittivity was 18. Embodiment 22

After adding ITO particles (made by Sumitomo Metal) 5weight % by ITO conversion in the solution obtained in Embodiment 9, by bar coater (No.7), membranes were formed on the PET board, it dried for 30 minutes at 120 \*\* in it, and the 0.2-micrometer-thick film was obtained in it. This film was irradiated with ultraviolet radiation for 10 minutes with the high pressure mercury lamp. Membranous field resistance was 350ohm/\*\*. Embodiments 23-28

the titania prepared like acrylic silicon resin (Kaneka ZEMURAKKUYC3918) and Embodiment 3 -- sol was mixed by each ratio shown in the 5th table, and the toluene solution of 10 weight % (sum total of resin-solid-content weight and the weight converted into titanium oxide) of solids concentration was prepared. The coat of this solution was carried out to various substrates by bar coater (No.12), and the hybrid film

was obtained. The characteristics of the obtained film were summarized in the 5th table, and were shown. The transparent hybrid film was obtained altogether.

## Comparative example 4

As titanium oxide, membranes were formed by the same operation as Embodiment 19 except having used titanium tetraisopropoxide. The result is collectively shown in the 5th table. The film whitened and a transparent film was not obtained.

第5表

,	基板 樹脂固形分重量/酸化		外観	密着性
		チタンに換算した重量		
実施例23	ガラス基板	80/20	透明	良好
実施例 2 4	ガラス基板	50/50	透明	良好
実施例25	ガラス基板	30/70	透明	良好
実施例26	PET基板	80/20	透明	良好
実施例27	PET基板	50/50	透明	良好
実施例28	PET基板	30/70	透明	良好
比較例4	ガラス基板	50/50	白濁	剥離

# Industrial applicability

[ by using the dispersoid which has a metal-oxygen bond by a kind of the metal oxide sol of this invention, as stated above ] Since uniform and transparent organic inorganic composite and a metal oxide film can be manufactured and such a substance is widely used as an optical material etc., it can be said that the industrial utility value of this invention is high.

[Brief Description of the Drawings]

Fig. 1 is a figure showing the UV characteristics of the low-temperature hydrolyzate of titanium alkoxide of Embodiment 1.